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FLUID-BED PRETREATMENT OF BITUMINOUS COALS  
AND LIGNITE AND DIRECT HYDROGENATION  
OF THE CHARS TO PIPELINE GAS

by

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ABSTRACT

The fluid-bed pretreatment of low-rank coals in nitrogen, air, carbon dioxide and steam atmospheres was investigated in a bench-scale unit at atmospheric pressure, and at maximum temperatures of 400° to 720°F, in a study of the production of non-agglomerating, reactive chars suitable for fluid-bed hydrogenation to pipeline gas. Reactivities of the chars in respect to methane and ethane production were determined in batch hydrogenation tests at 1350°F, approximately 17 standard cubic feet of hydrogen per pound of char and approximately 3000 psig maximum pressure.

The results of this study indicated that the optimum pretreatment temperature is 600°F for bituminous coal and 500°F for lignite, and that there is little variation in the reactivity of the chars produced in nitrogen, air and steam atmospheres. The chars produced in a carbon dioxide atmosphere showed consistently lower reactivity. Substantial agglomeration during pretreatment or hydrogasification occurred only with high-volatile bituminous coal. The extent of agglomeration increased with increases in pretreating temperature, and in steam and carbon dioxide atmospheres. Under the routine test conditions, the chars produced 50 to 55 weight percent (moisture-ash-free) of pipeline gas containing 70 to 80 mole percent of methane plus ethane upon reaching a hydrogasification temperature of 1350°F. At higher hydrogen/char ratios, substantially higher conversions of pretreated lignite were attained.

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Studies of methods for supplementing base-load natural gas requirements have indicated that conversion of coal to high-methane content gas, in areas where long-distance transmission lines pass through coal fields near the major market areas, may be the most economical method for transporting this source of energy to the domestic consumer in readily usable form. One method for the production of pipeline (900 Btu/SCF\*) gas is direct hydrogenation of low-rank coals to methane.<sup>3,4,5,7-11,27</sup> In such a process, the residual char may be used for hydrogen production by suspension-gasification with steam and oxygen, or for meeting fuel requirements. Essentially complete hydrogasification of lignites and some sub-bituminous coals may also be feasible; in this case hydrogen could be produced by reforming of product gas or of a relatively small portion of the primary natural gas supply.

Hydrogasification has three major advantages over the production of pipeline gas by the two-step partial coal oxidation-synthesis gas methanation process:<sup>1,24</sup> (1) large reduction, or potential elimination, of oxygen requirements, (2) elimination of the extreme synthesis gas purification requirements prior to catalytic methanation and (3) greater thermal efficiency through reduction of exothermic heats of reaction.<sup>28</sup> These potential advantages should constitute adequate justification for attempting to determine whether the design of a hydrogasification reactor suitable for large throughput rates, and with facilities for residual char removal, is feasible. On the basis of batch reactor tests, engineering studies and operation of pilot plant-scale models, it appears that the optimum design requires fluid-bed operation with parallel upward flow of dry pulverized coal and hydrogen at temperatures of 1300° to 1400°F and pressures of more than 1000 psig. A thorough knowledge of the agglomeration and hydrogasification characteristics of available coal feeds would be essential for successful operation of such a reactor.

In the first phase of this investigation, it was demonstrated in batch reactor tests that essentially olefin-free gases containing 60 to 80 volume percent methane could be produced by hydrogasification of an Illinois bituminous coal,<sup>28</sup> a Wyoming subbituminous coal and North Dakota lignite at 1350°F and 2500 to 3500 psig. By adjustment of hydrogen/coal ratios, gasifications on an ash- and moisture-free basis up to 80 weight percent were obtained with bituminous coal, and over 90 weight percent with lignite. It was also noted that after

- Standard cubic foot at 60°F, 30 inches of mercury pressure, saturated with water vapor.

preheating of these coals in the batch reactor to 600° to 700°F at atmospheric pressure in a nitrogen atmosphere, substantially higher rates of high heating value gas production were obtained at the expense of converting a relatively small portion of the coal to low heating value gases during pretreatment. However, the residues obtained at the end of hydrogasification were agglomerated, the degree of agglomeration being most severe with bituminous coal. Since this would be detrimental to the smooth operation of a continuous fluid-bed hydrogasification unit, the need for a pretreatment step yielding non-agglomerating, reactive chars was indicated.

Much of the published information useful in selecting pretreatment conditions has been obtained in the development of processes for the production of smokeless fuels, and in studies of upgrading of high-moisture content, low-rank coals for power plant, carbonization and metallurgical uses.<sup>16,20-23,25</sup> Of particular interest are the results of investigations concerned with reducing the caking or agglomeration tendencies of coal. For this purpose, thermal pretreatment at temperatures up to 800°F for partial removal of volatile constituents, often in the presence of an oxidizing atmosphere, is generally practiced.<sup>6,17,19,25</sup> Control of agglomeration by dilution with recycle char<sup>15</sup> and with inert solids<sup>13</sup> has also been recommended. Preheating in inert atmospheres before hydrogenation has been found to result in the elimination of a considerable fraction of the oxygen content in the form of carbon oxides, thereby raising the "available" hydrogen content of the coal.<sup>29</sup>

The effects of temperature, residence time and atmosphere on the quantity and composition of the gas evolved in the distillation of low-rank coals have been investigated extensively.<sup>12,14</sup> These studies show that as the temperature is raised, oxygen-containing substances break down to form water, carbon dioxide and carbon monoxide. Highest rates of carbon dioxide evolution occur between 400° and 600°F. As temperatures are increased further, hydrocarbon and hydrogen evolution represents the major portion of the increasing gas yields from bituminous and subbituminous coals; lignites tend to evolve mainly carbon oxides.

A considerable volume of literature also exists on pretreatment of coal with various acids, acid salts, nitric oxide, sulfur or sulfur compounds and caustic prior to hydrogenation.<sup>18</sup> However, the relative effects of these chemical pretreatment procedures on coal reactivity are not clearly defined.

#### APPARATUS AND PROCEDURE

The laboratory-scale coal pretreatment unit used in this study consisted of a pyrex fluid-bed retort, 1-3/4 inches inside diameter and 30-1/2 inches long with a 3-1/8 inch inside diameter, 15-inch long disengaging section. The retort closure was equipped with an 11/32 inch outside diameter thermocouple well which protruded very nearly to the bottom of the reaction zone.

The retort was heated by two circular electric furnaces. The lower one was 5 inches inside diameter and 12 inches long and had a rating of 2.5 kilowatts; the upper one was 2-3/8 inches inside diameter and 12 inches long and had a rating of one kilowatt. The disengaging section was heated with an electro-thermal tape. The unit was also equipped with a cyclone separator and a water-cooled condenser. A diagrammatic sketch of the apparatus is shown in Fig. 1.

Three-quarter pound batches of powdered coal (88-98 weight percent through 100-mesh) were dried at 110°C according to ASTM method D 271-48;<sup>2</sup> the dry coal was charged to the reactor at room temperature and was heated to the desired temperature at a rate of about 12°F per minute.

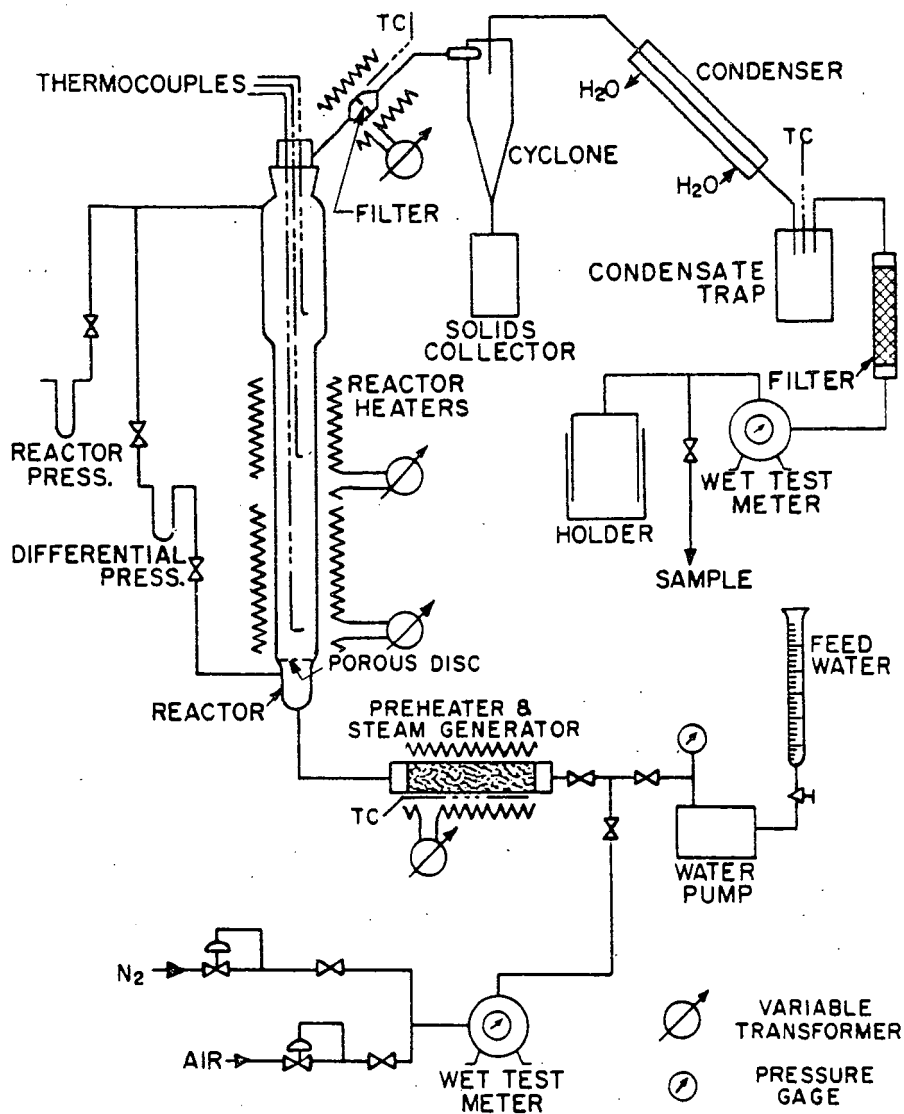


Fig. 1.-FLOW DIAGRAM OF FLUID-BED COAL PRETREATMENT LABORATORY UNIT

Measured volumes of nitrogen, air, carbon dioxide or steam, at rates sufficient to keep the coal bed in a fluidized state, were preheated in an electric furnace to 800° to 1000°F and introduced at the bottom of the retort.

Temperatures at the bottom, center and upper zones of the retort were sensed with chromel-alumel thermocouples and measured by a Wheelco temperature indicator. Pressures were read from a 15-inch standard mercury manometer.

The feed gases used as fluidizing media together with the fixed gas evolved from the distillation of the coal charge were passed through a 60-millimeter outside diameter fritted glass disc kept at 400°F, and a cyclone separator, to remove the suspended coal particles from the outgoing gas. The gas, after passing through a water-cooled condenser, was measured by wet-test meter and was stored in a gas-holder. Simultaneous readings of temperatures, pressures and volumes of inlet and outlet gases were recorded at intervals throughout the progress of the run.

Gas samples were taken at intervals by bleeding the sample into an evacuated 200 cc gas analysis bottle. At the conclusion of the run, the electric current was shut off and a composite gas sample was taken from the gas holder. After the retort cooled, it was opened and the solid residue recovered. The weights of the liquid condensate and of the solid residue were recorded.

Product gas samples were analyzed with a Consolidated Engineering Co. Model 21-103 mass spectrometer and specific gravities and heating values were calculated from the analyses. Product gas volumes and heating values were calculated for the conditions of 60°F, 30 inches of mercury absolute pressure and saturation with water vapor, assuming the ideal gas law. Specific gravities were calculated on a dry basis from the average molecular weight of the gas referred to air of molecular weight 28.972.

Since the gas samples taken at intervals during the test period differed in composition, the properties of the composite sample taken from the gas-holder at the end of the run were used to determine the weight fraction of the coal charge gasified during pretreatment. The material balance was calculated from the weights of liquid and solid products obtained at the end of the run, and from the weight of the fixed gas (total weight of outlet gas less the total weight of the feed gas) collected in the gas-holder.

The solid residue was subjected to a screen analysis to determine the extent of agglomeration and was analyzed in accordance with ASTM method D 271-48.

An average sample of the residue from pretreatment was crushed to minus 60-mesh and was charged to a one-liter capacity batch hydrogasification reactor to determine the gas yields and compositions obtainable at 1350°F and about 3000 psig, employing a hydrogen/char ratio of about 17 SCF/lb. The apparatus and procedure employed in the hydrogasification tests were described previously.<sup>2a</sup>

Solid residues obtained in these tests were again subjected to screen analyses to determine the extent of agglomeration.

#### YIELDS AND CHARACTERISTICS OF FLUID-BED PRETREATMENT PRODUCTS

The proximate, ultimate and screen analyses of the pulverized coals used in the pretreatment studies are shown in Table 1. Before charging to the bench-scale fluid-bed unit the samples were dried at 110°C. The product yields and compositions after pretreatment for 50 to 75 minutes in nitrogen, air, carbon dioxide and steam at flows of 4 to 6 SCF/lb dry coal-hour and at maximum temperatures of 400° to 720°F, are summarized in Table 2.

Table 1.-PROXIMATE, ULTIMATE AND SCREEN ANALYSES OF COALS  
USED IN TESTS

<u>Coal</u>	High- Volatile "B"	Subbitu- minous "A"	<u>Lignite</u>
Proximate Analysis, wt %			
Moisture	4.1	11.0	22.0
Volatile Matter	34.6	38.7	29.0
Ash	6.2	4.7	8.1
Fixed Carbon	55.1	45.6	40.9
Total	100.0	100.0	100.0
Heating Value, Btu/lb (Dry Basis)			
	13,790	12,760	10,800
Ultimate Analysis, wt % (Dry Basis)			
Ash	4.70	5.30	10.40
Carbon	72.50	66.60	65.30
Hydrogen	4.57	4.65	4.29
Sulfur	1.16	2.46	0.31
Nitrogen + Oxygen (By Difference)	17.07	20.99	19.70
Total	100.00	100.00	100.00
Screen Analysis, wt %			
+ 40 Mesh	0.1	--	--
+ 60 Mesh	2.5	0.8	1.0
+ 80 Mesh	0.9	1.0	1.0
+100 Mesh	8.4	--	0.1
+120 Mesh	9.1	3.2	2.7
+200 Mesh	20.7	5.9	9.6
-200 Mesh	58.3	89.1	85.6
Total	100.0	100.0	100.0



### Fixed Gases

In all of the runs the cumulative volume of fixed gas evolved increased with increases in pretreatment temperature as illustrated by the steam atmosphere data for lignite and bituminous coal shown in Fig. 2. The evolved gases consisted primarily of carbon dioxide in case of lignite and subbituminous coal, and of gaseous hydrocarbons and hydrogen in case of bituminous coal. After attainment of constant temperature, the rate of gas evolution decreased markedly with residence time as shown in Fig. 3 for steam atmosphere runs with lignite and bituminous coal at maximum pretreatment temperatures of 520°F and 620°F, respectively.

The effects of pretreatment atmosphere on the rate of fixed gas evolution from bituminous coal at approximately 600°F maximum pretreatment temperature are shown in Fig. 4. Carbon dioxide evolution was lowest in a steam atmosphere, probably as a result of substantial carbon monoxide formation, and was very rapid in an air atmosphere after attainment of maximum temperature. The highest hydrocarbon evolution occurred in a steam atmosphere and the lowest hydrocarbon evolution occurred in an air atmosphere.

Carbon dioxide evolution for subbituminous coal and lignite was higher than from bituminous coal in all of the pretreatment atmospheres investigated. Total carbon dioxide evolution for subbituminous coal in the 600°F runs was approximately 0.5 SCF/lb (dry basis) and carbon dioxide evolution from lignite in the 500°F runs was about 0.3 to 0.4 SCF/lb (dry basis). Hydrocarbon evolution for these relatively high oxygen content coals under the above conditions was low and normally ranged from 0.1 to 0.2 SCF/lb (dry basis) with the hydrocarbon formation being even lower in an air atmosphere.

### Residual Chars

The chars showed relatively uniform decreases in volatile matter with increases in pretreatment temperature, independently of other pretreatment conditions (Table 2); the effects of pretreating atmosphere composition on the quantity and composition of fixed gases evolved were not reflected in the proximate analyses. The ultimate analyses of selected chars (Table 2) also showed little variation with pretreatment conditions in the 500° to 700°F temperature range. However, the extent of agglomeration varied considerably with the composition of the pretreatment atmosphere as well as with pretreatment temperature. This is shown in Fig. 5 which indicates a well-defined trend of increases in agglomeration with increases in temperature for the pretreatment of bituminous coal in a steam atmosphere, and a tendency for considerably greater agglomeration in carbon dioxide and steam atmospheres as compared to nitrogen and air atmospheres. The greater agglomeration of bituminous coal in steam and carbon dioxide appeared to be related to the large evolution of hydrocarbon gases under these pretreatment conditions.

In contrast to this behavior, subbituminous coal and lignite did not agglomerate significantly over the entire range of pretreating conditions. This follows the trend of decreases in agglomeration with decreases in hydrocarbon evolution. However, subbituminous coal and lignite exhibited some tendency towards increased agglomeration at the higher temperatures, and in steam and carbon dioxide atmospheres.

In all the pretreatment runs, the amount of dried coal converted to gases was quite small (2.5 to 9.9 weight percent of charge). The heating values of the total product gases was low, normally less than 200 Btu/SCF, except in steam pretreatment runs in which gases with heating values in the 200 to 1000 Btu/SCF range were evolved.



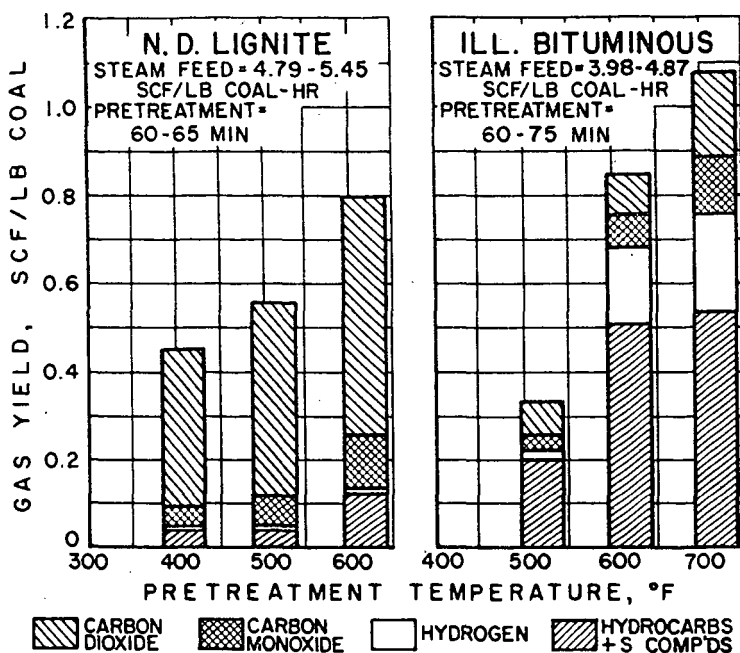


Fig. 2.-COMPOSITION AND YIELD OF GASES FROM FLUID-BED PRETREATMENT OF DRIED LIGNITE AND BITUMINOUS COAL IN STEAM

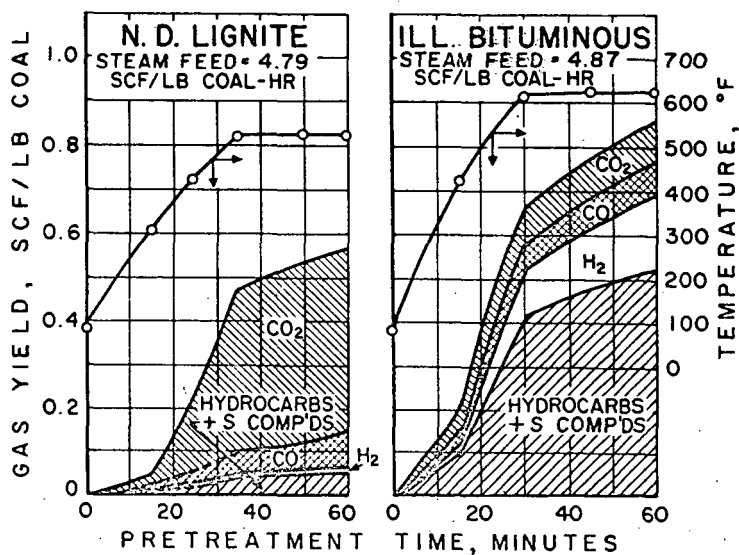


Fig. 3.-RATE OF EVOLUTION, AND COMPOSITION, OF GASES FROM FLUID-BED PRETREATMENT OF DRIED LIGNITE AND BITUMINOUS COAL IN STEAM

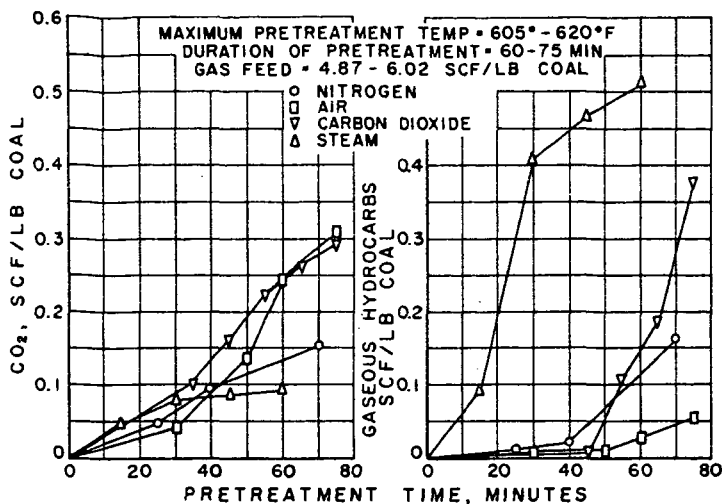


Fig. 4.-EFFECT OF GAS ATMOSPHERE ON RATE OF EVOLUTION OF CARBON DIOXIDE AND GASEOUS HYDROCARBONS FROM DRIED ILLINOIS HIGH-VOLATILE "B" BITUMINOUS COAL

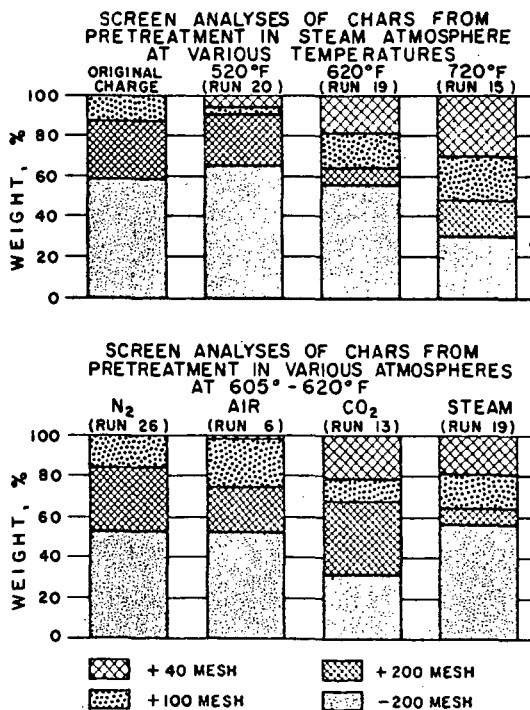


Fig. 5.-EFFECTS OF PRETREATMENT TEMPERATURE AND GAS ATMOSPHERE ON PARTICLE SIZE DISTRIBUTION OF DRIED ILLINOIS HIGH-VOLATILE "B" BITUMINOUS COAL

## HYDROGENOLYSIS CHARACTERISTICS OF PRETREATED COAL

The reactivities of the chars in respect to gaseous hydrocarbon formation were evaluated in batch hydrogasification tests. Test conditions were: 1000 to 1010 psig initial hydrogen pressures at room temperature, approximately 60-gram sample size, 1350°F maximum reaction temperature and 25 minutes run duration at maximum temperature. These charge quantities corresponded to a hydrogen/coal ratio of 17 SCF/lb and gave maximum reactor pressures of 2900 to 3300 psig (Table 3). The char charge to the reactor was obtained by sampling the residual chars from the pretreatment runs with a small riffle sampler and crushing to minus 60-mesh size.

The threshold temperatures reported in Table 3 correspond to the point at which the number of moles of gas in the reactor passed through a maximum due to initiation of the hydrogenolysis reactions. Reactor pressures increased nearly linearly with increases in temperature up to the threshold temperature (approximately 950° to 1050°F) and passed through a maximum at temperatures of 1100° to 1200°F. As the reactor attained the maximum run temperature, the pressures decreased rapidly and then continued to decrease at a lower rate during the remainder of the run. These characteristics of batch hydrogenolysis were similar to those reported previously.<sup>2a</sup>

### Effects of Pretreatment Conditions on Hydrogenolysis Yields

It can be observed from Table 3 that the net Btu recoveries and gaseous hydrocarbon yields for each of the three coals investigated fell within relatively narrow limits because of the similarity in char properties. (Net Btu Recovery is defined as the product of gas yield and heating value, minus the initial hydrogen heat of combustion.) However, there was a clear indication that optimum conversion to hydrocarbons at the time the reactor attained 1350°F occurred with bituminous and subbituminous coal chars prepared at 600°F, and with lignite char prepared at 500°F. Further, when comparing the results with the chars prepared at these optimum temperatures in the four different atmospheres (nitrogen, air, carbon dioxide and steam) the net Btu recoveries of the chars prepared in a carbon dioxide atmosphere were lower for each of the three coals.

These data indicate that the occurrence of optimum pretreatment conditions insofar as hydrogasification yields are concerned are the result of two factors: (1) increase in reactivity of the char to a maximum value as pretreatment temperature is increased, followed by reactivity decrease as low-temperature carbonization temperatures are approached and (2) continuous decrease in the content of relatively easily hydrogenable materials as pretreatment temperature is increased. The increased quantities of coal converted to liquid products with increases in pretreatment temperature (Table 2) are an indication of the loss of the more reactive coal constituents which eventually offsets any general increase in reactivity due to pretreatment.

In Fig. 6 the rates of methane-plus-ethane production from 720°F air-pretreated, and from dried bituminous coal, are compared. It can be seen that at least ten additional minutes of residence time at 1350°F would be required for the dried coal to yield product gases similar to those obtained with pretreated coal at the time the reactor attained 1350°F. In Table 4 the effects of steam and air pretreating on hydrogasification rates are shown for bituminous coal and lignite. The increase in the reactivity of the bituminous coal is illustrated by the fact that a gas of 67.5 mole % methane plus ethane content was produced from the pretreated sample (Run 112) upon attainment of a reactor temperature of 1275°F, or 15 minutes before reaching the maximum reaction temperature of 1350°F, whereas

Table 3.-HYDROGASIFICATION CHARACTERISTICS OF PRETREATED COALS

Coal No.	HIGH-VOLATILE "B" BITUMINOUS				SUBBITUMINOUS				LOW-VOLATILE			
	128	130	129	127	126	125	124	123	122	121	120	119
Pretreatment Conditions												
Gas Type												
Operating Conditions												
Pretreated Charge, gms./lb.	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
Hydrogen/Coal Ratio, SCF/lb.	17.1	16.9	16.9	16.9	16.9	16.9	16.9	16.9	16.9	16.9	16.9	16.9
Reactor Pressure, psig	2970	2970	2970	2970	2970	2970	2970	2970	2970	2970	2970	2970
Reactor Temperature, °F	1350	1350	1350	1350	1350	1350	1350	1350	1350	1350	1350	1350
Operating Results												
Product Gas Yield, Total SCF/lb	6.945	6.925	6.925	6.925	6.925	6.925	6.925	6.925	6.925	6.925	6.925	6.925
Net Moisture-Ash Free Coal Charge	14.61	14.26	14.73	14.46	14.78	14.78	14.78	14.78	14.78	14.78	14.78	14.78
Net Moisture-Ash Free Coal Charge	11.4	11.5	11.6	11.5	11.5	11.5	11.5	11.5	11.5	11.5	11.5	11.5
Net Moisture-Ash Free Coal Charge	51.0	51.2	51.1	50.4	46.2	48.9	56.0	58.9	58.9	58.9	58.9	58.9
Net Moisture-Ash Free Coal Charge	100.6	100.4	102.5	98.4	99.0	99.5	101.0	99.2	98.2	98.2	98.2	98.2
Composition, Mole %												
CO + CO <sub>2</sub>	2.5	2.5	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
H <sub>2</sub>	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
CH <sub>4</sub>	17.3	15.3	19.8	19.8	23.8	28.4	18.0	18.0	18.0	18.0	18.0	18.0
C <sub>2</sub> H <sub>6</sub>	77.3	79.5	70.9	75.2	71.6	67.6	71.8	76.4	73.6	74.6	74.9	75.2
C <sub>3</sub> H <sub>8</sub>	—	—	—	—	—	—	—	—	—	—	—	—
C <sub>4</sub> H <sub>10</sub>	—	—	—	—	—	—	—	—	—	—	—	—
Balances	—	—	—	—	—	—	—	—	—	—	—	—
Clorine	—	—	—	—	—	—	—	—	—	—	—	—
Toluene	—	—	—	—	—	—	—	—	—	—	—	—
Specific Gravity, Air = 1	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Reactor Properties, wt %												
+100 - Wash	9.5	19.2	9.0	11.1	27.2	22.1	12.8	20.8	18.8	13.4	6.7	11.4
+200 - Wash	11.8	22.8	6.2	15.0	1.8	19.7	19.3	23.8	28.4	16.2	4.9	18.5
+400 - Wash	88.1	45.6	65.8	68.1	32.9	68.1	61.3	48.9	43.0	58.2	80.0	55.7

1. Initial H<sub>2</sub> pressure 1000-1010 psig except for Run 106 in which it was 1200 psig.

2. At the time reported reactor temperature was reached (zero residence time at 1350°F).

3. 100 wt % of Product Gas - wt % of Hydrogen in Moisture-Ash Free Pretreated Coal Charge

4. Based on product gas volume calculated from reactor pressure, volume and temperature.

5. SCF - Gas volume in standard cubic feet at 60°F, 30 inches of mercury pressure and saturated with water vapor.

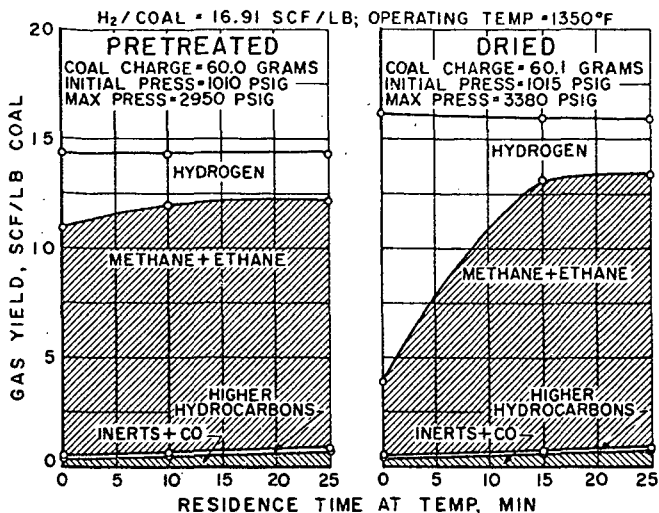
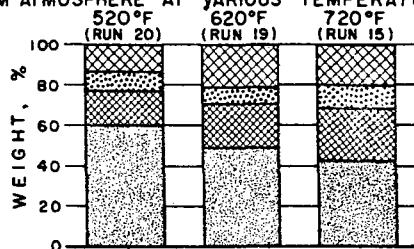


Fig. 6.-EFFECT OF RESIDENCE TIME ON HYDROGASIFICATION YIELDS FROM DRIED AND PRETREATED (AIR AT  $720^\circ\text{F}$ ) ILLINOIS HIGH-VOLATILE "B" BITUMINOUS COAL

SCREEN ANALYSES OF RESIDUES FROM  
HYDROGASIFICATION OF CHAR PRETREATED IN  
STEAM ATMOSPHERE AT VARIOUS TEMPERATURES



SCREEN ANALYSES OF RESIDUES FROM  
HYDROGASIFICATION OF CHAR PRETREATED  
IN VARIOUS ATMOSPHERES AT  $605^\circ\text{--}620^\circ\text{F}$

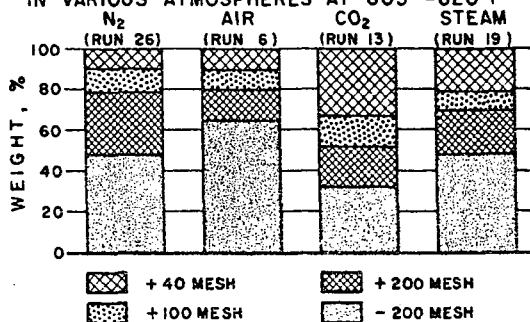


Fig. 7.-EFFECT OF PRETREATMENT TEMPERATURE AND GAS ATMOSPHERE ON PARTICLE SIZE DISTRIBUTION OF RESIDUES FROM HYDROGASIFICATION OF ILLINOIS HIGH-VOLATILE "B" BITUMINOUS COAL CHAR

in the comparable test with the dried coal (Run 67) the product gas contained only 21.1 mole % methane plus ethane at the time a reactor temperature of 1350°F was attained.

#### Pretreatment Losses

Because of evolution of substantial amounts of gaseous hydrocarbons and of liquid products during pretreatment of bituminous coal (Table 2) the increase in reactivity to hydrogenation was accompanied by a decrease in ultimate gaseous hydrocarbon yield and net Btu recovery. However, a substantial portion of these pretreatment losses can be recovered in the form of fuel gases produced during pretreatment; steam pretreatment of bituminous coal yields high heating value product gases suitable for addition to the pipeline gas formed in the hydrogasification step. Further, pretreatment is essential in reducing or eliminating agglomeration of coking or caking coals to be used as feeds to moving-bed or fluid-bed hydrogasification processes so that pretreatment losses must be considered a characteristic of bituminous coal operation.

The effects of steam pretreatment on the hydrogasification product distribution for dried Illinois high volatile "B" bituminous coal are illustrated by Runs 67 and 112, Table 4. Net Btu recoveries and gas yields are reported on an as received basis as well as on the basis of the actual dried or pretreated coal charge to permit direct comparisons of the results. It can be seen that for approximately equal product gas compositions (after 25 minutes at 1350°F for the dried coal and at 0 minutes at 1350°F for the pretreated coal) substantially higher conversions were obtained with the dried coal. A clearer picture of the relative yields with and without pretreatment can be gained from the following data summary based on 100.0 weight units of moisture-ash-free bituminous coal and on char or residue yields corrected to 100% material balance (the lower conversion of the pretreated coal was probably in part due to the somewhat lower hydrogen/coal ratio employed):

<u>Pretreatment</u>	<u>Steam, 620°F</u> <u>(Run PR-19)</u>	<u>None</u>
<u>Product</u>		
Char (Moisture-Ash-Free)	90.4	--
Net Water and Other		
Condensates	4.4	--
CO, CO <sub>2</sub>	1.8	--
Hydrogen	Trace	--
Gaseous Hydrocarbons	3.4	--

<u>Hydrogasification</u>	<u>0 Minutes at 1350°F</u> <u>(Run 67)</u>	<u>25 Minutes at 1350°F</u> <u>(Run 112)</u>
<u>Feeds</u>		
Char or Coal (Moisture-Ash-Free)	90.4	100.0
Hydrogen	8.9	9.4
<u>Products</u>		
Residue (Moisture-Ash-Free)	43.1	39.8
Condensates	1.9	5.0
CO, CO <sub>2</sub> , N <sub>2</sub>	3.4	4.7
Hydrogen	1.5	1.4
Gaseous Hydrocarbons	49.4	58.5

Table 4.-COMPARISON OF OPERATING CONDITIONS AND RESULTS FOR HIGH-PRESSURE HYDROGASIFICATION OF DRIED AND PRETREATED SAMPLES OF BITUMINOUS COAL AND LIGNITE

Coal Run No.	Type of Pretreatment	ILLINOIS HIGH-VOLATILE "B" BITUMINOUS			NORTH DAKOTA LIGNITE		
		67	112	140	71	140	140
		Dried <sup>1</sup>	Dried and Steam Pretreated (520°F)		Dried <sup>1</sup>	Dried and Air Pretreated (520°F)	
As Received Coal Charge, gram		67.0	70.1		60.0	53.9	
Pretreated Charge, gram		60.1	60.0		45.1	40.0	
Operating Conditions							
Initial Pressure, psig		1015	1010		1025	1010	
Hydrogen/As Received Coal Charge Ratio, SCF/lb		15.17	14.36		17.42	19.23	
Hydrogen/Pretreated Coal Charge Ratio, SCF/lb		16.91	16.77		23.18	25.93	
Threshold Temperature, °F		1025	977		1025	964	
Time to Reach Threshold Temp., min		85	90	102	52	95	120
Total Time Elapsed, min		0	0	0	0	0	25
Run Time at Temperature, min		3200	3050	2990	3760	2890	2870
Reactor Pressure, psig		1350	1305	1350	1350	1350	1350
Reactor Temperature, °F							
Operating Results							
Net But Recovery (Based on As Received Coal Charge), Metu/lb		2.300	7.726	5.827	6.041	8.915	7.918
Net But Recovery (Based on Pretreated Coal Charge), Metu/lb		2.564	8.610	7.050	7.049	11.394	10.676
Product Gas Yield (Based on As Received Coal Charge), SCF/lb		14.47	14.34	13.43	13.17	18.87	16.35
Product Gas Yield (Based on Pretreated Coal Charge), SCF/lb		16.15	15.98	15.69	15.37	25.10	22.04
Gaseous Hydrocarbon Yield (Based on As Received Coal Charge), SCF/lb		3.12	11.62	9.13	9.39	11.45	13.18
Gaseous Hydrocarbon Yield (Based on Pretreated Coal Charge), SCF/lb		3.48	12.94	10.67	10.96	15.24	17.54
Gaseous Hydrocarbon Space-Time Yield, SCF/GF-hr		21.2	48.6	70.2	66.7	68.2	48.3
Coal Hydrogasified, wt %		18.5	55.2	50.7	50.2	50.9	51.8
Product Gas Properties							
Gas Composition, mole %							
N <sub>2</sub> +CO		1.4	2.5	3.8	3.5	4.2	3.6
CO <sub>2</sub>		0.6	0.8	0.9	0.7	0.7	0.4
H <sub>2</sub>		76.4	15.7	27.2	24.4	20.3	32.2
H <sub>2</sub> S		--	--	0.1	0.1	--	5.0
CH <sub>4</sub>		17.8	80.2	67.0	70.7	74.4	70.4
C <sub>2</sub> H <sub>6</sub>		3.3	0.3	0.5	0.4	0.2	0.1
C <sub>3</sub> H <sub>8</sub> plus Olefins		0.4	0.2	--	--	--	--
Benzene		--	--	0.1	--	0.2	--
Total		100.0	100.0	100.0	100.0	100.0	100.0
Heating Value, Btu/SCF		494	877	791	807	749	851
Specific Gravity, Air = 1		0.2160	0.5046	0.4569	0.4628	0.4656	0.4626

1. Dried according to ASTM Method D 271-48

2. Based on time after the reactor attained threshold temperature

3. 100 Wt of Product Gas - Wt of Hydrogen In Wt of Moisture-Ash Free Charge

SCF - Gas volume in standard cubic feet at 60°F, 30 inches of mercury pressure and saturated with water vapor.

The comparative performance of dried and air-pretreated (520°F maximum temperature) lignite is shown in Run 71 and 140, Table 4. In these runs the quantity of sample was reduced to correspond approximately to 60 grams on an as-received basis. This was done to demonstrate that essentially complete conversion of lignite to a high heating gas is possible at short residence times if sufficient amounts of hydrogen are provided. In spite of the high initial reactivity of the lignite, pretreatment resulted in further increases in reactivity although these increases were relatively small; methane plus ethane contents and gaseous hydrocarbon yields, upon attainment of 1350°F reactor temperature before and after pretreatment were 60.0 and 74.7 mole %, and 11.45 and 12.25 SCF/lb (as received basis), respectively. However, there were only minor differences in ultimate net Btu recoveries and gaseous hydrocarbon yields for the dried and pretreated lignite. The higher volumetric gas yields and weight percent hydrogasification yields for the dried lignite were primarily the result of substantial carbon dioxide evolution; the pretreated sample had already evolved most of the carbon dioxide prior to hydrogasification. Thus, it appears that the major benefit of lignite pretreatment would be the increase in product gas heating value (80 to 90 Btu/SCF on the basis of the data of Table 4), due to reduction of carbon dioxide content; increases in reactivity would probably not justify pretreatment and lignite has little agglomeration tendency. The behavior of subbituminous coal appeared to fall between that of bituminous coal and lignite on the basis of less complete data than presented for the other two coals.

#### Agglomeration of Hydrogasification Residues

One of the objectives of the hydrogenolysis tests with pretreated coals was to determine if variations in agglomeration of the hydrogasification residue could be related to pretreatment conditions. As noted before, a sample of the char from each pretreatment run was ground to minus 60-mesh to approximate constant initial conditions. Although this procedure was probably inadequate insofar as the size distribution of minus 60-mesh particles is concerned, it can be seen from Fig. 7 that the degree of agglomeration indicated by the percentage of plus 40-mesh particles in the hydrogasification residue followed the degree of agglomeration of dried bituminous coal during pretreatment (Fig. 5). Increases in pretreatment temperature resulted in increased agglomeration of the residue, and agglomeration during hydrogasification increased with various pretreatment atmospheres in the following order: air, nitrogen, steam and carbon dioxide.

#### Hydrogasification Characteristics of Low-Temperature Chars

An indication of the reactivities of low-temperature chars and cokes produced with the Bureau of Mines<sup>22,23</sup> and Disco<sup>15</sup> processes can be obtained by comparison of the batch hydrogasification test results shown in Table 5 with the data for the pretreated coals reported in Table 3. It can be seen that over 40 weight percent of these low-temperature carbonization products were converted to gases with heating values of 760 to 880 Btu/SCF at 1350°F and 2400 to 3100 psig, employing a hydrogen/charge ratio of 17 SCF/lb. Although the coal conversions in these tests are quite low, the data nevertheless serve to indicate the possibility of obtaining high-heating value gases from non-agglomerating chars from which a major portion of reactive coal constituents have been removed under the relatively severe pretreating conditions employed in low-temperature carbonization processes.



Table 5.-OPERATING RESULTS FOR THE HYDROGASIFICATION OF LOW-TEMPERATURE CHARs

Coal Run No. Source	BITUMINOUS CHAR		SUBBITUMINOUS CHAR		LIGNITE CHAR	
	82	84	84	85	85	85
	Pittsburgh Consolidation Coal Co.	U. S. Bureau of Mines	U. S. Bureau of Mines	U. S. Bureau of Mines	U. S. Bureau of Mines	U. S. Bureau of Mines
Proximate Analysis, wt %	0.9 Moisture; 21.2 Vol. Matter; 6.2 Ash 60.0	1.3 Moisture; 19.3 Vol. Matter; 4.6 Ash 60.0	1.9 Moisture; 25.2 Vol. Matter; 11.3 Ash 60.0			
Charge, gram						
Operating Conditions						
Initial Pressure, psig	1010	1010	1010	1010	1010	1010
Hydrogen/Coal Ratio, SCF/lb	16.91	16.83	16.83	16.83	16.83	16.83
Threshold Temperature, °F	875	745	790	790	790	790
Time to Reach Threshold Temp., min	36	31	31	36	36	36
Total Time Elapsed, min	90	100	94	104	100	125
Run Time at Temp., min	0	10	0	10	0	25
Reactor Pressure, psig	2430	2430	2690	2700	3060	3120
Reactor Temp. °F	1350	1350	1350	1350	1350	1350
Operating Results						
Net Btu Recovery, MBtu/lb	0.862	4.820	4.914	4.963	6.083	6.273
Product Gas Yield, Total SCF/lb	11.97	11.97	11.90	13.23	15.04	15.33
Gaseous Hydrocarbon Space-Time Yield, SCF/CF-hr	14.9	36.1	29.7	34.0	38.3	28.0
Net Moisture-Ash Free Coal Hydrogasified, wt % <sup>2</sup>	13.1	37.7	39.9	41.9	46.3	47.7
Material Balance, % <sup>3</sup>			98.2	102.2		98.5
Product Gas Properties						
Gas Composition, mole %						
N <sub>2</sub> + CO	1.5	2.5	2.9	5.2	5.4	5.6
CO <sub>2</sub>	0.3	0.3	0.3	1.6	1.0	0.8
H <sub>2</sub>	71.6	20.2	17.9	26.7	26.6	25.7
H <sub>2</sub> S	--	0.1	--	--	--	--
CH <sub>4</sub>	23.5	75.5	77.3	63.5	66.6	66.6
C <sub>2</sub> H <sub>6</sub> plus Olefins	2.7	0.7	0.2	2.4	0.1	0.1
Benzene	0.2	--	0.1	--	--	--
Toluene plus	0.1	--	0.1	--	--	--
Total	100.0	100.0	100.0	100.0	100.0	100.0
Heating Value, Btu/SCF	523	854	867	798	761	759
Specific Gravity, Air = 1	0.2333	0.4873	0.5118	0.4846	0.5185	0.4349

1. Based on time after the reactor attained threshold temperature. SCF - Gas volume in standard cubic feet at 60°F, 30 inches of mercury pressure and saturated with water vapor.

2. 100 Wt of Product Gas - Wt of Hydrogen In Wt of Moisture-Ash Free Charge

3. Based on product gas volume calculated from reactor pressure, volume and temperature.

## CONCLUSIONS

The results of this study indicated that a representative sub-bituminous coal and North Dakota lignite showed relatively little agglomeration when pretreated in a fluid-bed retort with 4 to 6 SCF/lb-hr of nitrogen, air, carbon dioxide and steam at temperatures of 400° to 600°F and atmospheric pressure. A high-volatile "B" bituminous coal agglomerated to an increasing degree with increases in pretreatment temperature from 500° to 700°F. This agglomeration tendency was greatest in carbon dioxide and steam atmospheres, and relatively small in air and nitrogen atmospheres. The amounts of fixed gases evolved (2.5 to 9.9 wt % of the dry charge) increased with increases in pretreatment temperature, and at any constant temperature, the rate of fixed gas evolution decreased with increases in residence time. The predominant constituents in the gaseous pretreatment products of the bituminous coal were paraffins and olefins, whereas the subbituminous coal and the lignite evolved primarily carbon dioxide.

Reactivities of the pretreated chars, as determined in batch hydrogasification tests at a maximum reactor temperature of 1350°F and a maximum pressure of approximately 3000 psig, first increased to an optimum value with increases in pretreatment temperature, and then decreased as a result of increased evolution of easily hydrogenable tar and other volatile combustibles. The optimum pretreatment temperature appeared to be 600°F for bituminous and subbituminous coal, and 500°F for lignite. Chars produced at constant pretreatment temperature in nitrogen, air and steam atmospheres showed little variation in reactivity. However, carbon dioxide-treated chars showed consistently lower reactivities than nitrogen, air and steam-treated chars.

The chars, in general, produced 50 to 55 weight percent of (moisture-ash-free basis) of pipeline gas containing 70 to 80 percent of methane plus ethane at the time 1350°F was reached when using a charge of approximately 17 SCF of hydrogen per pound of char. At higher hydrogen/char ratios, substantially higher weight percent conversions of lignite to gaseous hydrocarbons were obtained.

The particle size distribution of the residues obtained at the end of hydrogasification tests in general followed the trends of the pretreated chars. Steam and carbon dioxide treatments, and high pretreating temperatures, caused greater agglomeration during hydrogasification.

These data indicate that the production of non-agglomerating, reactive chars from lignite and subbituminous coal for fluid-bed hydrogenation to pipeline gas will be feasible. Although substantial agglomeration during pretreatment or hydrogasification was noted with bituminous coal, the data also show that chars suitable for conversion in a continuous fluid-bed hydrogenation unit could be produced by treating the bituminous coal in a fluid-bed at 600°F, in atmospheres of air, nitrogen and possibly steam.

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